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**Citation for published version:**

Heal, MR 2008, 'The effect of absorbent grid preparation method on precision and accuracy of ambient nitrogen dioxide measurements using Palmes passive diffusion tubes', *Journal of Environmental Monitoring*, vol. 10, no. 11, pp. 1363-1369. <https://doi.org/10.1039/b811230d>

**Digital Object Identifier (DOI):**

[10.1039/b811230d](https://doi.org/10.1039/b811230d)

**Link:**

[Link to publication record in Edinburgh Research Explorer](#)

**Document Version:**

Publisher's PDF, also known as Version of record

**Published In:**

Journal of Environmental Monitoring

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# The effect of absorbent grid preparation method on precision and accuracy of ambient nitrogen dioxide measurements using Palmes passive diffusion tubes

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Received 2nd July 2008, Accepted 1st September 2008

First published as an Advance Article on the web 1st October 2008

DOI: 10.1039/b811230d

A few studies have suggested that the precision and accuracy of measurement of NO<sub>2</sub> by Palmes-type passive diffusion tube (PDT) are affected by the method of preparation of the triethanolamine (TEA) absorbent coating on the grids. These studies have been quite limited in extent and have tended to evaluate PDT accuracy as zero bias between PDT NO<sub>2</sub> value and the exposure-averaged NO<sub>2</sub> determined by co-located chemiluminescence analyser. This ignores the well-documented intrinsic systematic biases on PDT-derived NO<sub>2</sub>, such as within-tube chemistry and exposure-duration nitrite loss, which may lead to non-zero bias values irrespective of effects of TEA absorbent preparation method on PDT accuracy. This paper reports on a statistical analysis of a large dataset comprising 680 duplicated PDT exposures spanning 146 separate exposure periods, spread over five urban exposure locations and a number of years. In each exposure period, PDTs prepared by between four and six different grid preparation methods were simultaneously compared. The preparation methods used combinations of the following: acetone or water as the TEA solvent; 20% or 50% as %TEA in the solution; and application of TEA solution by dipping grids for several minutes in the solution before drying and tube assembly, or by pipetting 50 µL of solution directly onto grids already placed in the PDT cap. These represent the range of preparation procedures typically used. Accuracy was evaluated as maximised nitrite capture within an exposure. Data were analysed by general linear modelling including examination of interaction between different aspects of grid preparation method. PDT precision and accuracy were both significantly better, on average, when the PDT grids were prepared by dipping in TEA solution, and neither solvent or %TEA used for the dipping solution were important. Where PDT preparation by pipetting TEA solution onto grids is to be used, better performance was obtained using 20% TEA in water. A systematic positive bias in PDT measure of NO<sub>2</sub>, consistent with within-tube oxidation of NO to NO<sub>2</sub> and independent of preparation method, was again evident in this work.

## Introduction

Nitrogen dioxide (NO<sub>2</sub>) is an air pollutant with adverse health associations<sup>1</sup> for which air quality objectives on ambient air concentration have been set in many countries. It is both directly emitted and the product of atmospheric oxidation of NO. However, despite increased controls on some source emissions of NO<sub>x</sub> (=NO + NO<sub>2</sub>), levels of NO<sub>2</sub> in many locations are only declining slowly, if at all.<sup>2,3</sup> As a consequence, measurement of ambient NO<sub>2</sub> remains a priority in air pollution management in order to identify where breaches in NO<sub>2</sub> objectives exist and to monitor the efficacy of mitigation action.

The reference method for ambient NO<sub>2</sub> measurement is the chemiluminescence analyser. However, in the UK, as elsewhere, the main approach for indicative assessment of ambient NO<sub>2</sub> is the deployment of Palmes-type passive diffusion tube (PDTs)<sup>4</sup> within extensive local authority networks.<sup>2</sup> No agreed standard

yet exists for PDT methodology so variations in the preparation of the triethanolamine (TEA) absorbent and in the post-exposure extraction and quantification of the captured nitrite from that originally proposed by Palmes *et al.*<sup>4</sup> have arisen in practice. Whilst it is accepted that NO<sub>2</sub> PDTs are not as accurate or as precise as continuous analysers, it is also recognised that these methodological differences may contribute to the observed variations in PDT results in intercomparison procedures.<sup>5</sup>

One aspect of the PDT method where there are clearly distinguishable differences in procedure between laboratories is in the preparation of the TEA-coated grids and a few studies have reported associated differences in the precision and accuracy of the NO<sub>2</sub> concentration.<sup>6–8</sup> The three main variations in PDT preparation are that the TEA absorbent may be dissolved in acetone or water as a solvent, that the concentration of TEA in the solvent may be 50% or 20% (sometimes 10%), and that the TEA is applied to the stainless steel grids either by submerging the grids in the TEA solution before removal and drying on absorbent tissue, or by pipetting a fixed volume (usually 50 µL) of the TEA solution onto two grids already inserted into an end cap. In one study,<sup>7</sup> three preparation

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methods (dipped 50% TEA in acetone, pipetted 50% TEA in water, pipetted 20% TEA in water) were compared over three exposures in a dosed tank environment; tubes prepared by pipetting 50% TEA in water on the grids yielded lower NO<sub>2</sub> than measured by the chemiluminescence analyser and the other PDT methods. Kirby *et al.*<sup>6</sup> compared tubes prepared by dipping 50% TEA in acetone or pipetting 10%, 20%, or 50% TEA in water over 10 exposure periods at a single urban background site and also concluded that tubes prepared by pipetting 50% TEA in water onto grids gave lower NO<sub>2</sub> capture (and were marginally less precise).

Both the above studies are based on a very small number of PDT exposures. Hamilton and Heal<sup>8</sup> were more comprehensive in their approach, simultaneously trialling eight different preparation method combinations in 80 exposures spread across three different exposure sites. They concluded that precision was poorer, on average, for pipetted application methods, and that pipetted methods were also more variable in accuracy. Preparation methods using 50% TEA in water led to particularly imprecise data. However, a shortcoming of this latter study was that pipetting was onto grids in caps into which the tube barrel had already been inserted, whereas the more general practice is to insert the tube barrel into the cap after the solution has been pipetted onto the grids.

Overall, systematic comparison of different PDT preparation methods remains very limited, particularly when the pipetting preparation data of Hamilton and Heal<sup>8</sup> are excluded as being unrepresentative of actual practice. The small numbers of exposure periods and the small numbers of different preparation methods trialled at any one time also do not allow investigation of interactions between the preparation variables.

A further important shortcoming of previous work has been equating PDT accuracy with zero bias between the NO<sub>2</sub> concentration derived from the PDT and from a co-located chemiluminescence analyser. There are good theoretical reasons, supported by observation, to expect intrinsic biases in PDT measurement, the net magnitude of which will differ with exposure location and exposure period, irrespective of any inaccuracy associated with PDT preparation method. Foremost amongst the intrinsic positive biases is within-tube chemical generation of additional NO<sub>2</sub> from co-diffusing NO and O<sub>3</sub>,<sup>9</sup> whose magnitude depends on the time-varying absolute and relative concentrations of the three species during the exposure.<sup>10,11</sup> This will be affected, amongst other factors, by distance of a particular PDT exposure location to strong sources of NO, *e.g.* busy roads. Secondly, positive bias due to shortening of the diffusion path length by wind-induced turbulence at the mouth of the tube,<sup>12</sup> if significant, is also likely to vary according to the exposure location and period. Similarly, intrinsic negative bias caused by exposure-duration dependent loss of captured nitrite may also vary with exposure location and time of year.<sup>11</sup> The net effect of these factors will vary according to the individual exposure environment, so it is erroneous to use tendency to zero bias as the metric for PDT accuracy, particularly when comparing results from different PDT exposures.

The work reported here overcomes these issues. It is a statistical analysis of PDT precision and accuracy of a large dataset of 146 separate PDT exposures in which PDTs prepared by at least four out of seven different grid preparation methods were

simultaneously exposed in duplicate during each exposure. The data are derived from a range of urban exposure locations, over a period of several years, and includes the work of several analysts. Because several combinations of preparation methods were trialled every exposure, it is possible to test for statistical interaction between different aspects of PDT preparation method; for example, does effect of solvent differ according to % solvent. Also, the assessment of PDT accuracy used here is independent of any exposure-related intrinsic bias in PDT NO<sub>2</sub>. The dataset includes the dipped (but not pipetted) methods data previously reported in Hamilton and Heal<sup>8</sup> but the other 732 PDT NO<sub>2</sub> data are unpublished.

## Methods

The acrylic diffusion tubes, polyethylene caps and stainless steel grids used for the PDT exposures described here were obtained from Gradko International. All components were re-used (subject to visual inspection of their continued integrity), but were cleaned thoroughly between use with detergent solution and deionised water. Tube physical dimensions (mean  $\pm$  95% CI from measurement of a sub-sample) were length  $7.1 \pm 0.1$  cm, internal cross-section area  $0.92 \pm 0.02$  cm<sup>2</sup>.

The dataset of PDT NO<sub>2</sub> measurements comprises PDT exposures at five different sites in Edinburgh. Three are classified as roadside (Haymarket, Castle St. and Queen's St.), one as urban central (the former AURN site at Princes St. Garden) and one as urban background (the relocated AURN site at St. Leonard's). The median (min–max) exposure-averaged NO<sub>2</sub> concentrations across all sites, as measured by co-located chemiluminescence analysers, was 39.3 (13.2–86.5)  $\mu\text{g m}^{-3}$ . The exposures were spread intermittently over a period of more than five years between November 2001 and February 2007. Over this period four different analysts prepared and analysed the PDTs, always following exactly the same written protocols. The fact that different analysts have contributed to the dataset presented here emulates the real-world situation in which different laboratories and analysts contribute to monitoring network data.

PDT preparation methods under trial comprised different combinations of the two different 'levels' of each of the following three preparation method 'factors':

(1) Factor 'Application Method,' with levels 'dipped' (grids coated with TEA by soaking them for 10 min in the appropriate solution of TEA followed by drying of the grids on tissue and tube assembly with two grids per tube) or 'pipetted' (grids coated by pipetting 50  $\mu\text{L}$  of the TEA solution onto two stainless steel grids already placed in a cap followed by completion of tube assembly);

(2) Factor 'Solvent', with levels 'acetone' or 'water';

(3) Factor '%TEA' (in solvent), with levels '20%' or '50%'.

For the methods in which grids were prepared by pipetting, the solution of TEA was spread as evenly as possible around the grid surface with a spreading action of the pipette tip.

Duplicates of PDT preparations were deployed in every PDT exposure. These provide %RSD (relative standard deviation) data for evaluation of precision. Although all PDT exposures were co-located with a chemiluminescence analyser, for the reasons given in the introduction %BIAS of PDT with respect to the analyser is not used here for evaluation of PDT accuracy.

Instead, the following measure of accuracy was adopted. For any given exposure location and exposure period all co-located PDTs should be subject to the same intrinsic biases of within-tube generation of NO<sub>2</sub>, wind-induced shortening of diffusion path length, and exposure-duration reduction in nitrite. Since the goal of diffusion tube methodology is to attain stoichiometric trapping of NO<sub>2</sub> arriving at the absorbent into nitrite then, other things being equal, greater PDT-derived NO<sub>2</sub> concentration in a given exposure equals greater PDT accuracy. (PDT-derived NO<sub>2</sub> concentration is a direct proxy for nitrite captured.) The method of preparing grids by dipping in solutions of 50% TEA in acetone was trialled in every exposure in this dataset. Therefore accuracy of PDT preparation method is evaluated using the CAPTURE metric, where  $\text{CAPTURE} = \%[(\text{duplicate mean PDT NO}_2 \text{ for prep. method X})/(\text{duplicate mean PDT NO}_2 \text{ for prep. method dipping, acetone, 50\% TEA})]$ . Lower values, on average, of CAPTURE is indicative of poorer accuracy, on average.

Regardless of their method of preparation, all PDTs were subsequently handled equivalently and analysed in the same way to quantify the nitrite trapped in the absorbent during exposure. The nitrite was first extracted into 1.5 mL of deionised water *in-situ* in the tube, and then 1.65 mL of acidified mixed sulfanilamide : NEDA solution (in reagent mass ratio 1 : 0.007) added to form the diazo chromophore. Absorbance intensity was measured at 540 nm in a dual beam UV/vis spectrometer using solution from an equivalently-treated blank tube (*i.e.* reagents present but zero nitrite) in the reference beam. Independent duplicate sets of nitrite calibration standards were prepared for each analysis. The average ambient NO<sub>2</sub> concentration during the exposure was calculated from the nitrite calibration graphs using 0.154 cm<sup>2</sup> s<sup>-1</sup> as the diffusion coefficient of NO<sub>2</sub> in air. This is the value of diffusion coefficient originally recommended by Palmes *et al.*<sup>4</sup> and used for many years throughout the UK national and local authority NO<sub>2</sub> PDT networks. Recently the UK Working Group on NO<sub>2</sub> PDT harmonisation, referring to work by Massman,<sup>13</sup> has recommended 0.146 cm<sup>2</sup> s<sup>-1</sup> as the value for the diffusion coefficient appropriate to a UK average ambient temperature of 284 K.<sup>5</sup> However, because it is necessary to report measured concentrations of NO<sub>2</sub> in mass units at the EU standard reporting temperature of 293 K (particularly when comparing PDT data to chemiluminescence data which are likewise reported at a temperature of 293 K), the NO<sub>2</sub> mass concentration derived using this diffusion coefficient must be subsequently temperature corrected by a factor 284/293 = 0.969.<sup>5</sup> The net effect of both these corrections can be achieved in one step using a diffusion coefficient value of 0.151 cm<sup>2</sup> s<sup>-1</sup>. Application of the updated specification for the diffusion coefficient would increase each value of PDT-derived NO<sub>2</sub> concentration used in this paper by ~2%, but would have no effect on the evaluation of PDT precision and accuracy *via* %RSD and CAPTURE since both are relative values.

The total dataset available comprises 680 duplicated PDT exposures spanning 146 separate exposure locations and periods. There are almost no missing data within this total: seven missing %RSD values because of loss of one or more replicate tube, and three missing CAPTURE values where both replicates are missing. The dataset has not been 'cleaned' of very poor %RSD values, all of which remain included.

Of the eight possible combinations of tube preparation factors and levels, the preparation method of pipetting 20% TEA in acetone was not trialled since this method has not been reported in the literature nor used by any of the labs in the UK PDT networks. For the seven other combinations of tube preparation factors and levels under investigation, not all were compared in every exposure period, since this would have involved an excessive number of parallel deployments, but each exposure always consisted of a minimum of four, and up to six, of the possible combinations. (Average number of different preparation methods trialled per exposure period = 680/146 = 4.7). There is an imbalance in the dataset in number of exposures associated with each possible preparation combination, ranging from 146 exposures for each of the two preparation methods 50% TEA in acetone, dipped, and 50% TEA in water, dipped, to 30 exposures for the preparation method 20% TEA in water, pipetted. Importantly, however, all seven tested preparation methods were trialled by at least two of the four analysts which reduces the possibility that any observed differences in NO<sub>2</sub> measurement between differently-prepared PDTs are driven solely by an analyst-associated cause.

All PDT exposures were for one week. While this does not emulate the majority practice of UK networks, which is for one month exposures, it is not considered to be relevant to the data analysis, as both %RSD and CAPTURE are expressed relative to other PDT values in the same exposure. In fact, an advantage of one week exposures is that the confounding effect of decreasing PDT NO<sub>2</sub> values with exposure duration, which may well be variable, should be minimised.<sup>11</sup>

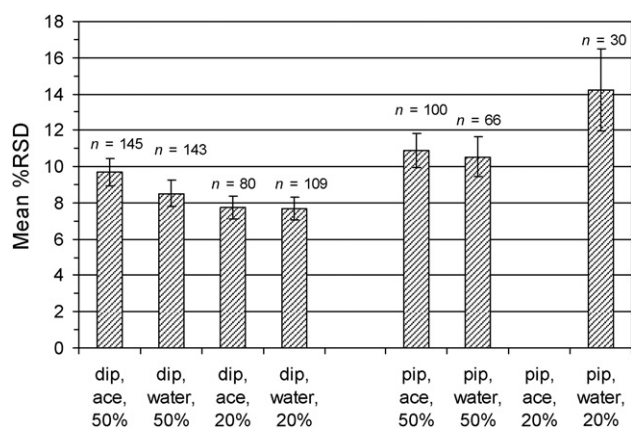
General linear modelling (GLM) in Minitab v.14 was used to test for significant factors acting on the two dependent variables %RSD and CAPTURE being investigated. The full GLM comprised: (a) the three factors 'Application Method', 'Solvent' and '%TEA' as the main-effect fixed factors under test; (b) the three pairwise combinations of these factors to test for significant interactions; (c) the two factors 'Analyst' and 'Exposure site' as additional main-effect random factors *i.e.* factors not under specific experimental test, but which might also have influence on the dependent variables. There were insufficient combinations of trials to examine for interaction between 'Analyst' and the three main factors under test. The extent of interaction between the three main test factors was examined closely since it is important to check whether a non-significant main effect of a factor results from two opposing trends of a second factor in combination with the first factor.

Regardless of the significance values of the two random factors 'Analyst' and 'Exposure site', the GLMs were repeated with one or both of these factor designations removed from the model in order to examine whether this led to any difference in the interpretation of the effects of the fixed factors on the dependent variables.

## Results

### Evaluation of preparation method on precision

The mean %RSD values for all exposures of each preparation technique investigated are illustrated in Fig. 1. The *p* values associated with terms in the GLM of the total %RSD dataset are



**Fig. 1** Mean ( $\pm\sigma$ ) of duplicate %RSD for all PDT exposures of each preparation method investigated. The number of %RSD data contributing to each mean value is given above each bar.

**Table 1** GLM  $p$ -values associated with the effects of named factors and factor interactions on PDT precision as assessed by the %RSD values for duplicate exposures. Terms significant at the  $p < 0.05$  level are highlighted in bold

Term	Full model	Model excluding site as factor	Model excluding site & analyst as factors
Analyst	<b>0.006</b>	<b>0.015</b>	—
Exposure site	0.331	—	—
Application	<b>0.000</b>	<b>0.000</b>	<b>0.000</b>
Solvent	0.152	0.151	0.196
%TEA	0.905	0.904	0.579
Application + solvent	0.658	0.654	0.637
Application + %TEA	0.104	0.103	<b>0.037</b>
Solvent + %TEA	0.403	0.403	0.310

given in Table 1. The GLM confirms the expectation that PDT precision is independent of the exposure location, so Fig. 2 shows the main and interaction effects plots for the model in which exposure site is not a specified factor.

Fig. 1 shows that PDTs prepared by dipping grids in solution are more precise, on average, than PDTs prepared by pipetting the solution onto grids in caps. The high significance associated with this observation is confirmed in Table 1 and Fig. 2. In contrast, there is no evidence of significant differences in PDT precision for either acetone or water as the solvent or for either 20% or 50% TEA composition. Analyst is a significant factor which reflects the reality that different analysts differ in the quality of their precision. However, the difference in precision between analyst is smaller than the difference in precision associated with application method. Since different analysts trialled different combinations of preparation method factors and levels, the significant analyst term should not unduly influence the interpretations of the effects of the fixed factors under test.

The above interpretations of the effects of the main factors on precision are not compromised by the presence of significant interactions between the main factors. There is some trend towards better dipped method precision with 20% TEA in solvent and better pipetted method precision with 50% TEA in

solvent, but the effect is small compared with the difference in precision between dipped and pipetted methods.

### Evaluation of preparation method on accuracy

The mean CAPTURE values for each preparation method are illustrated in Fig. 3 and the  $p$ -values derived from application of the GLMs to the data are summarised in Table 2. These show significantly greater nitrite capture, taken to represent greater accuracy, on average, for PDTs in which grids are prepared by dipping rather than by pipetting. Dipped method PDT  $\text{NO}_2$  values are also more significantly correlated with the corresponding chemiluminescence analyser data than those from the pipetted methods (values not reported), a metric which is also interpreted as indicating better performance of a PDT method (although still subject to distortion because of different intrinsic PDT biases in different exposure situations).

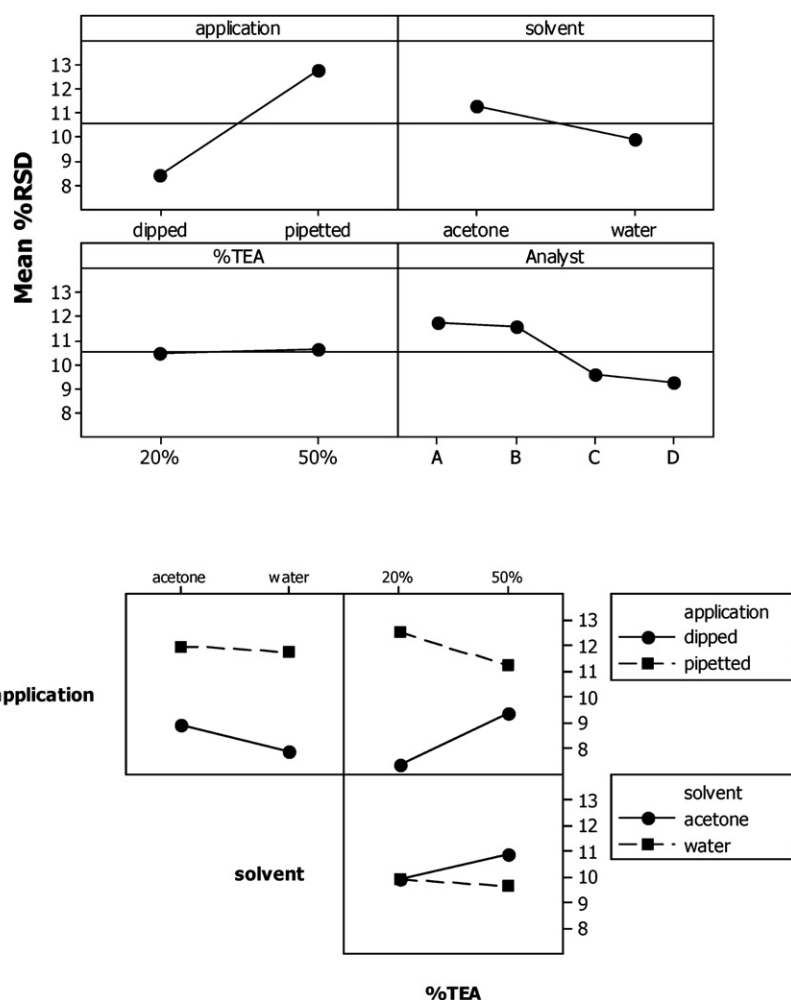
Exposure location is not a significant factor which supports the rationale for use of the CAPTURE metric for evaluation of accuracy. (Exposure location is a significant factor in a GLM using %bias as the dependent variable.) Analyst is a significant factor. This cannot be due to systematic differences between analysts in the nitrite extraction and calibration part of the  $\text{NO}_2$  determination since any such error would influence all nitrite analyses for a given exposure period equally. Instead the significant influence of analyst is a consequence of the different distributions between analysts of preparation methods trialled. This is not relevant to a statistical analysis of CAPTURE values so the main and interaction effects plots shown in Fig. 4 are for the model, excluding site and analyst as factors.

The data show that, as for precision, accuracy is not influenced by the solvent. Accuracy is significantly influenced by %TEA but this needs to be interpreted in the context of significant interaction: greater accuracy is associated with 20% TEA solutions when coating grids by pipetting but accuracy is not influenced by %TEA when coating grids by dipping.

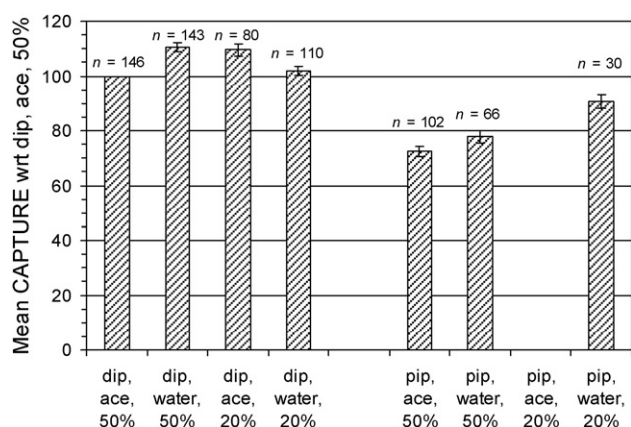
### Discussion

A consistent picture emerges from the statistical evaluation of both precision and accuracy. Dipped preparation methods provide both better precision and greater nitrite capture (interpreted here as greater accuracy), on average, than do pipetting preparation methods. Neither precision or nitrite capture is influenced by use of either acetone or water as the solvent. There is a significant trend for 20% TEA composition to yield greater nitrite capture than 50% TEA composition in pipetting methods, but %TEA is not an important factor for nitrite capture in dipping methods nor for precision for any method trialled. The observation of lower nitrite capture when pipetting with higher %TEA solution is consistent with the earlier smaller trials.<sup>6,7</sup>

The conclusions from this study are supported by a recent analysis by Air Quality Consultants Ltd of data from PDT exposures co-located with chemiluminescence analysers accumulated from local authorities around the UK.<sup>14</sup> These authors applied five different quantitative and semi-quantitative measures of PDT precision and accuracy to a dataset comprising 161 annual co-location studies, involving 21 laboratories, to try and tease out which of several variations in PDT preparation and



**Fig. 2** Results of application of a general linear model to PDT precision data (%RSD values) that incorporates application method, solvent and %TEA as fixed-effect factors, analyst as a random-effect factor and the pairwise interactions of the three fixed-effect factors. Main effects are illustrated in the upper panels and interactions in the lower panels.

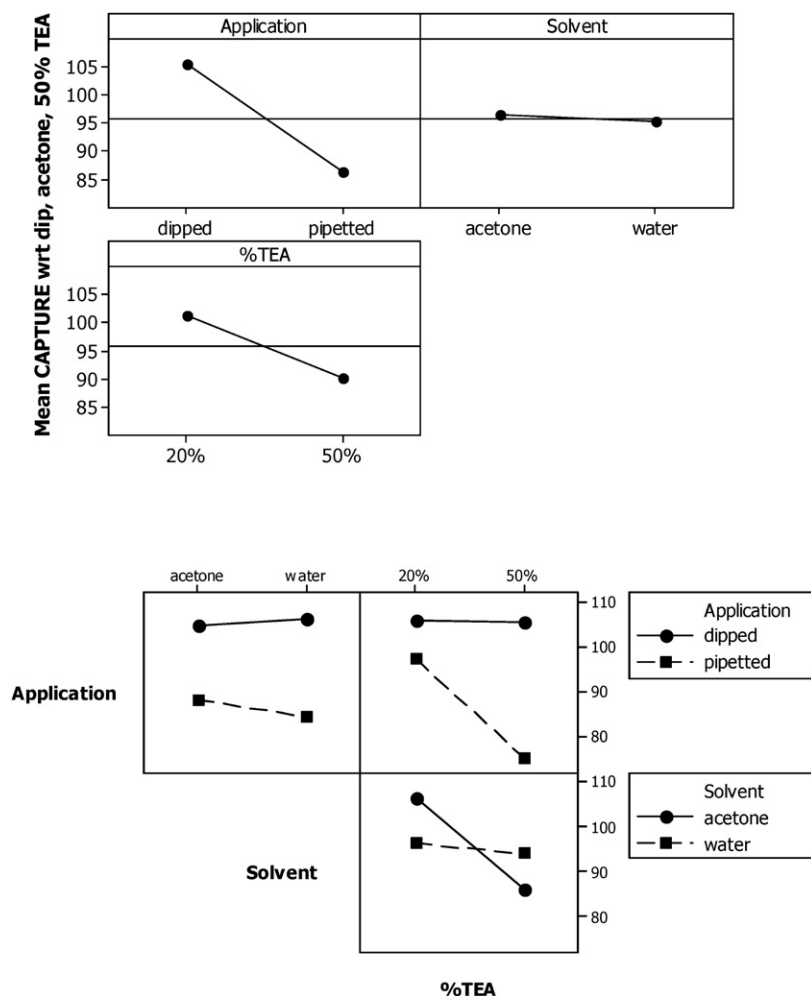


**Fig. 3** Mean ( $\pm\sigma$ ) of the CAPTURE metric for all PDT exposures of each preparation method investigated. All values of CAPTURE for the PDT preparation method dipping in 50% TEA in acetone are 100% by definition. The number of CAPTURE data contributing to each mean value is given above each bar.

analysis methodology used by the laboratories led to better overall PDT performance. In respect of issues associated with variations in PDT preparation method the following were concluded (using Laxen *et al.*'s<sup>14</sup> phrasing): some evidence that dipping of grids provides a better performance than tubes

**Table 2** GLM *p*-values associated with the effects of named factors and factor interactions on PDT accuracy as assessed by the CAPTURE values (the PDT NO<sub>2</sub> value relative to the NO<sub>2</sub> derived from the PDT prepared by dipping, 50% TEA in acetone, in the same exposure). Terms significant at the *p* < 0.05 level are highlighted in bold

Term	Full model	Model excluding site as factor	Model excluding site & analyst as factors
Analyst	<b>0.000</b>	<b>0.000</b>	—
Exposure site	0.141	—	—
Application	<b>0.000</b>	<b>0.000</b>	<b>0.000</b>
Solvent	0.971	0.971	0.511
%TEA	<b>0.000</b>	<b>0.000</b>	<b>0.000</b>
Application + solvent	0.274	0.274	0.113
Application + %TEA	<b>0.000</b>	<b>0.000</b>	<b>0.000</b>
Solvent + %TEA	<b>0.000</b>	<b>0.000</b>	<b>0.000</b>



**Fig. 4** Results of application of a general linear model to PDT accuracy data (represented here by the CAPTURE metric) that incorporates application method, solvent and %TEA as fixed-effect factors and the pairwise interactions of the three fixed-effect factors. Main effects are illustrated in the upper panels and interactions in the lower panels.

prepared by pipetting onto grids; a clear pattern that tubes prepared with grids soaked for 10 min or more performed better than tubes prepared with grids dipped for less than 1 min; a clear pattern that tubes prepared with grids that have been dried before assembly perform better than those with grids that are wet when the tube is assembled; and a clear pattern that tubes prepared using 20% TEA in water perform better than those using 50% TEA in acetone. A caveat on the last conclusion is that the dataset did not include preparation methods with 20% TEA in acetone or 50% TEA in water. Also, these workers' analysis could not examine for interaction between %TEA, solvent and grid application technique.

It is to be expected that poorer nitrite capture efficiency is associated with the same method(s) that give poorer precision. Given there is a physical upper limit to the amount of nitrite that can be captured, then greater variability in nitrite capture must lead to lower capture efficiency, on average.

The poorer performance of pipetting methods revealed in this and the Laxen *et al.*<sup>14</sup> analyses is likely driven, at least in part, by variability associated with different analysts' approaches to execution of the pipetting technique, as compared with the likely

smaller inter-analyst variability associated with execution of the dipping technique. The latter is essentially analyst independent, *i.e.* TEA coverage *via* surface tension followed by drying. Thus, for a single lab/analyst, it may well be possible to obtain pipetted method precision to match dipped method precision. Even so, Gerboles *et al.*<sup>15</sup> reported substantial sensitivity of PDT precision to whether a pipetted solution (of 10% TEA in water) was spread all across the grid surface compared with the same volume pipetted as a single drop in the centre of the grids.

In addition to greater variability in analyst technique, pipetting methods may lead to poorer precision and nitrite capture because of greater variability in both amount and coverage of TEA coating caused, perhaps, by less even coverage of grids from pipette dispensing, less absolute amount of TEA added to grids in pipetted solution compared with coating by dipping, loss of viscous TEA sticking to pipette tip, and handling of assembled tubes before the grids are thoroughly dry leading to dribbling of TEA solution down tube walls. Pipetting solutions of TEA in acetone will be particularly subject to variability because of the difficulty of consistently drawing up and dispensing a solution comprised of such a volatile solvent.

Although not the primary focus of the study, it is relevant to report that the PDT-derived NO<sub>2</sub> concentrations in this work were larger, on average, than the corresponding one week exposure-averaged NO<sub>2</sub> measured by chemiluminescence analyser (although, as has been demonstrated, the extent of positive bias varied with different PDT preparation method). For example, median bias across all sites for PDTs prepared by dipping grids in 50% acetone was 26% ( $n = 140$ , bias values not available for six exposures because of missing analyser data). The median bias for this method for individual sites varied between 17% ( $n = 52$ ) at the Haymarket site to 57% ( $n = 22$ ) at the Queen's Street site. For comparison, the median exposure-averaged analyser NO<sub>x</sub>/NO<sub>2</sub> ratio was 2.1 across all sites, and 2.2 and 2.0 for the Haymarket and Queen's Street sites, respectively. The data therefore provide further evidence of intrinsic over-read of NO<sub>2</sub> by PDT consistent with within-tube oxidation of a proportion of the NO also present at the exposure location,<sup>10,11,16</sup> and confirms the problem of using zero bias as a measure of accuracy.

## Conclusions

Accumulated evidence clearly points towards greater consistency, *i.e.* method robustness, on average, in PDT precision and accuracy when the PDT absorbent grids are prepared by thoroughly soaking in TEA solution and subsequent drying before tube assembly. The proportions of TEA and solvent used for the solution are not important, although it is strongly recommended that only a single solvent-%TEA combination is specified in preparation protocols for the sake of harmonisation and standardisation. Where PDT preparation by pipetting TEA solution onto grids pre-installed into caps is retained as a method, it is strongly recommended that this should be a standardised volume (*e.g.* 50 µl) of a solution of 20% TEA in water. The findings from this work support the instructions for permitted PDT absorbent grid preparation methods recently issued to UK laboratories.<sup>5</sup>

A systematic positive bias in PDT measure of NO<sub>2</sub>, consistent with within-tube oxidation of NO to NO<sub>2</sub> and independent of preparation method, is again evident in this work.

The above conclusions are independent of any variation in PDT NO<sub>2</sub> measurement that may be caused by variation in the procedure used for extraction and quantification of trapped nitrite after PDT exposure. It is recommended that this aspect of NO<sub>2</sub> PDT methodology also be evaluated.

## Acknowledgements

The assistance in laboratory work over a number of years from students in the School of Chemistry, University of Edinburgh, is gratefully acknowledged, as are Janet Brown and colleagues from the City of Edinburgh Council for access to exposure locations and provision of chemiluminescence analyser data.

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